

OBSERVATIONS ON THE RARE EARTHS

I. THE REDUCTION OF EUROPIUM TO THE DIVALENT STATE

II. STUDIES ON THE CHEMICAL REDUCTION OF YTTERBIUM

BY

WILBERT AUGUST TAEBEL

B.S., Elmhurst College, 1935

M.S., University of Illinois, 1936

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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URBANA, ILLINOIS

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OBSERVATIONS ON THE RARE EARTHS

PART I.

THE REDUCTION OF EUROPIUM TO THE DIVALENT STATE

The striking similarity of the members of the rare earths group in chemical and physical properties has made the separation and purification of any one member a long and arduous task.

The characteristic valence of the rare earths is three. Certain members, however, may be made to assume a valence of two; others that of four. The utilization of the "anomalous valence" states of the rare earths has proven to be one of the most effective means of isolating individual members. This has been particularly true with cerium, europium, and ytterbium.

Divalent europium was discovered by Urbain and Bourion¹ in 1911. Jantsch and co-workers² resumed the investigation of europous compounds. They comment on the insoluble nature of the sulfate. Yntema,³ in 1930, realized the significance of this property. He was able to isolate europium by first reducing it electrolytically, followed subsequently by its precipitation as the sulfate. Pearce,⁴ Kleene,⁵ Marsh,⁶ and Brukl⁷ have studied the separation of europium.

Recently, McCoy⁸ has prepared europous sulfate by simply reducing the trichloride by means of a modified Jones reductor and running the resulting solution into one containing sulfate ion. He does not claim quantitative removal. Previous investigations⁵ in this laboratory indicated that the method possessed an efficiency of 85-90 per cent.

A chemical means of reducing europium, followed by a quantitative removal as the sulfate would be desirable. Both europium and ytterbium may be reduced electrolytically. Consequently if rare earth solutions are electrolyzed in the presence of sulfate ion both members are precipitated. A chemical method which would reduce europium but not ytterbium would enable one to remove these members independently of each other.

It was found that europium could be reduced quantitatively to the divalent state by means of a modified Jones reductor. The optimum conditions for the removal of the sulfate was determined. Using solutions containing 3 mg. of europium ion per ml., which were 0.05 N in HCl; a rate of flow of 5 ml. per minute; an

inert atmosphere of nitrogen; 6 N sulfuric acid as the precipitating medium; strontium sulfate as a co-precipitating agent; and a temperature of 25°C. it was found possible to approach quantitative removal of europium by means of a modified Jones reductor.

PART II

STUDIES ON THE CHEMICAL REDUCTION OF YTTERBIUM

Klemm and Schüth⁹ discovered divalent ytterbium in 1929. Ball and Yntema¹⁰ applied the method of separating europium to the isolation of ytterbium. Marsh,¹¹ Hopkins and co-workers,¹² Prandtl,¹³ and Brukl¹⁴ have studied the electrolytic method of separating ytterbium from rare earth mixtures.

The resistance to reduction increases in the order: europium, ytterbium, samarium. Ytterbium, therefore, would be the most likely member to interfere with the determination and removal of europium. Exhaustive studies indicated that ytterbium could not be reduced by means of the Jones reductor. Elements below calcium in the electromotive series are not strong enough reducing agents, under the conditions studied, to reduce ytterbium to the divalent state.

Liquid amalgams of sodium, barium, and strontium reduce ytterbium to a valence of two. This property was investigated as a possible means of separating ytterbium from rare earth mixtures. Under the conditions investigated, the method is only approximately 50 per cent as efficient as the electrolytic method.

BIBLIOGRAPHY

- ¹Urbain and Bourion, *Compt. rend.*, **153**, 1155 (1911).
²Jantsch, Alber, and Grubitsch, *Monatsh.*, **53-54**, 304 (1929).
³Yntema, *J. Am. Chem. Soc.*, **52**, 2782 (1930).
⁴Pearce, Master's Thesis, University of Illinois, 1931.
⁵Kleene, Master's Thesis, University of Illinois, 1935.
⁶Marsh, *J. Chem. Soc.* (1934) 1972.
⁷Brükl, *Angew. Chem.*, **49**, 159 (1936).
⁸McCoy, *J. Am. Chem. Soc.*, **57**, 1756 (1935).
⁹Klemm and Schüth, *Z. anorg. allgem. Chem.*, **184**, 353 (1929).
¹⁰Ball and Yntema, *J. Am. Chem. Soc.*, **52**, 4264 (1930).
¹¹Marsh, *J. Chem. Soc.*, (1937) 1367.
¹²Pearce, Naeser, and Hopkins, *Trans. Electrochem. Soc.* Vol. LXIX (1936).
¹³Prandtl, *Z. anorg. allgem. Chem.*, **209**, 13 (1932).
¹⁴Brükl, *Angew. Chem.*, **50**, 25 (1937).

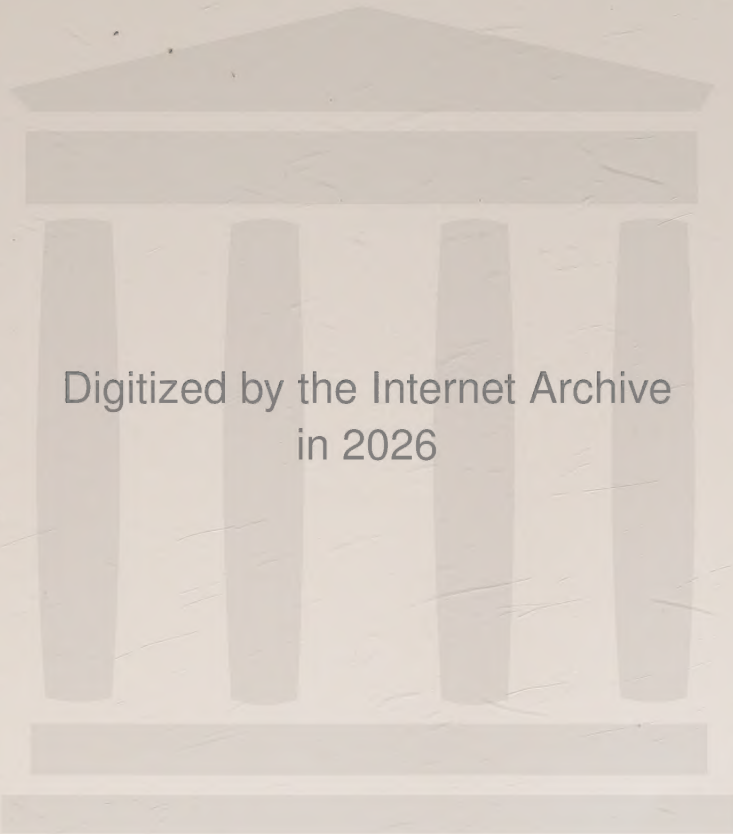
VITA

The author was born in Chicago, on April 18, 1907. He received his elementary education in Illinois and Wisconsin, and was graduated from Glenbard High School, Glen Ellyn, Illinois, in June, 1926. He obtained the Bachelor of Science degree from Elmhurst College, Elmhurst, Illinois, graduating with summa cum laude honors in June, 1936.

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He is a member of the American Chemical Society, Inorganic and Physical Division, Sigma Xi, Phi Lambda Upsilon, and Phi Kappa Phi. He is co-author of the following publications:

- B S. Hopkins and W. A. Taebel. The Rare Earths as Catalysts, Trans. Electrochem. Soc. Vol. LXXI (1936).
- W. A. Taebel and B S. Hopkins. Observations on the Rare Earths, The Preparation of the Anhydrous Rare Earth Iodides, Z. anorg. allgem. Chem. 235, 62 (1937).
- B S. Hopkins and W. A. Taebel. Progress in the Analysis of the Rare Earth Group, Trans. Ill. State Acad. Sci. (Forthcoming.)



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